Characterization of Coupled Hydrologic-Biogeochemical Processes using Geophysical Data

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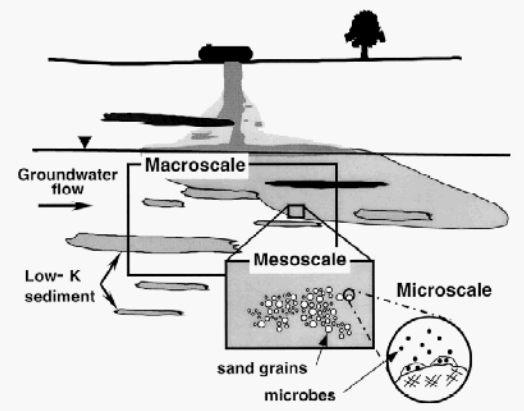
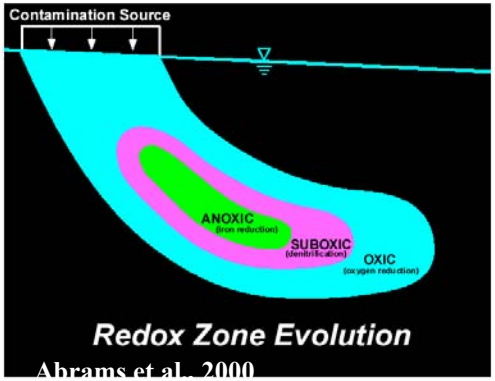
- **Project Conception:** Problem Statement & Previous Research
- **EMSP Project 86922: New Start**
  - Objectives
  - Current Experiment
  - Expected Project Results

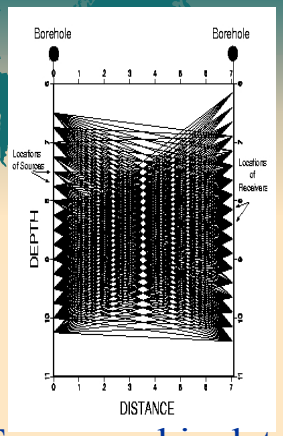
Statement of the Problem

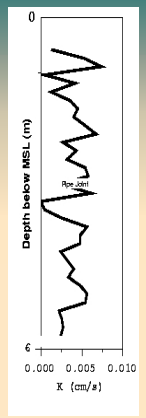
- **Large spatial and temporal variability of hydrogeological-biogeochemical parameters in natural systems renders characterization/monitoring of subsurface processes difficult;**





- **Conventional field characterization and monitoring techniques are often inadequate:**
  - Difficulty in getting information about **horizontal** or **field-scale** variability;
  - Requires **drilling, which disturbs** subsurface and is **prohibitive in contaminated** areas.
- **As a consequence, characterization/monitoring is insufficient at the field scale:**
  - **Remediation** schemes can be unnecessarily **expensive, ineffective, or difficult to assess** away from treatment well(s)
  - Inadequate data available to investigate **coupled processes *AT THE FIELD SCALE***.
- **Investigate potential of geophysical methods for monitoring system transformations and for understanding coupled processes…..**



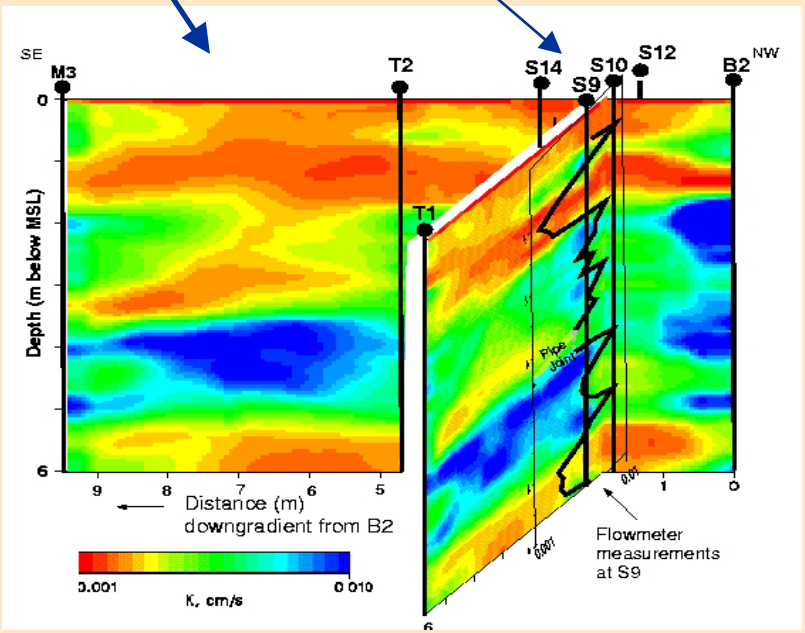


Tomographic data

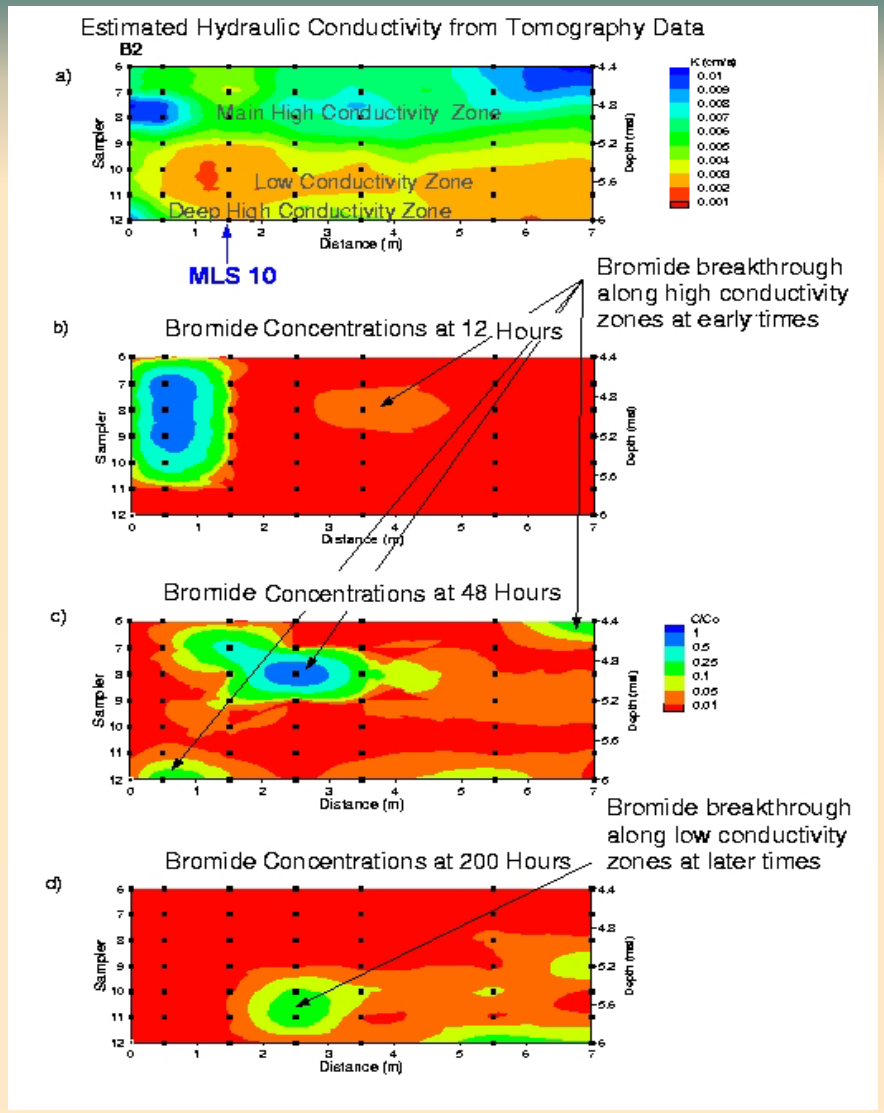
Log data

Background:

Field-Scale Hydrogeological Characterization using Geophysical Data



1/4m by 1/4 resolution

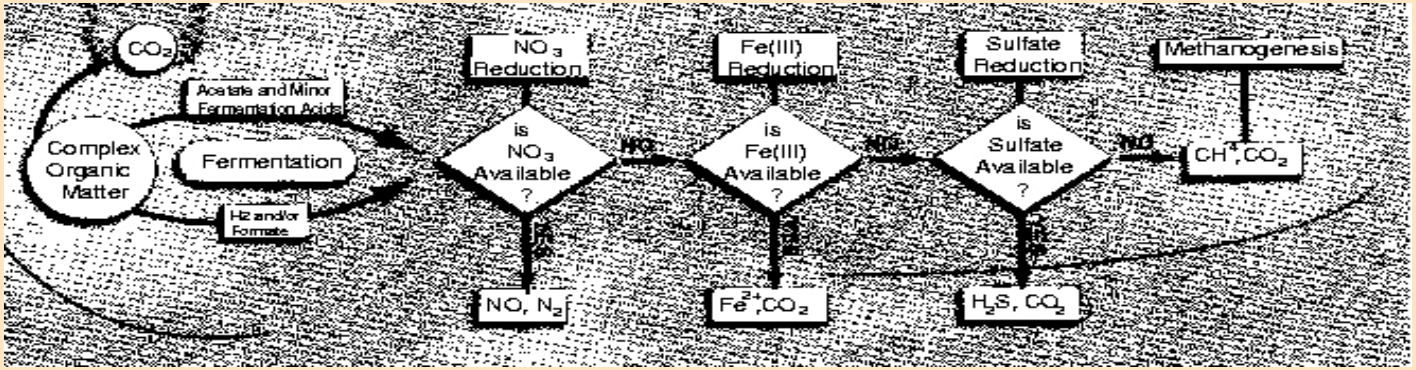


Hubbard et al., WRR 37(10), 2001

*Tomography Estimates useful for **improving chemical transport predictions** (Scheibe et al., Ground Water, 2003) and for **understanding bacterial transport** as a function of hydrogeological heterogeneity (Mallioux et al., WRR, 2003).

Moving Forward: Monitoring System Transformations during Remediation using Geophysical Data

- Many remediation approaches also induce **system transformations (gas, biofilm and precipitation formation)**
- These processes are **dynamic, complex, and coupled**



Chapelle, 2000

- Extremely difficult to understand using wellbore data
- ***Investigate utility of geophysical methods for providing information about system transformations over space and time***
  - ***Radar, Seismic and Electrical Methods***
  - ***Lab and Field Scale***

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Expected Geophysical Signatures associated with Reaction Products & Hydrogeological Heterogeneity

Examples of Reactions associated with remediation treatments:

- Organic Carbon + Electron Acceptor + Nutrient $\Rightarrow$ Biomass + CO_2 + other
- DOC + NO_3 $\Rightarrow$ CH_2O (biomass) + CO_2 + N_2
- Chlorinated Solvent + Permanganate $\Rightarrow$ Precipitate + CO_2 +Anions
- DOC + SO_4 $\Rightarrow$ Biomass + Sulfide

Examples of geophysical responses to reaction products and hydrogeology:

Geophysical Method	Geophysical Attribute	Gas Evolution	Precipitation Formation	Biofilm Formation
Radar	**Velocity**	*Increase*	*Increase*	*Increase (?)*
	Amplitude	*Increase*	*Variable*	*Increase?*
Seismic	**Velocity**	*Decrease*	*Increase*	*Increase*
	Amplitude	*Decrease*	*?*	*?*
Electrical	**Conductivity**	*Decrease*	*Variable*	*Increase*

Preliminary Lab Experiment: using Seismic Amplitudes to detect gas generation

Reduction of NO_3^- ⟶ N_2

Electron Donor: Nitrate

Carbon Source: Acetate

Microbe: *Pseudomonas Stutzeri* (courtesy PNNL)

Grown to ~2 x 10^7 cells/gram sand and suspended in a nutrient depleted growth media

***Cross-column seismic measurements**

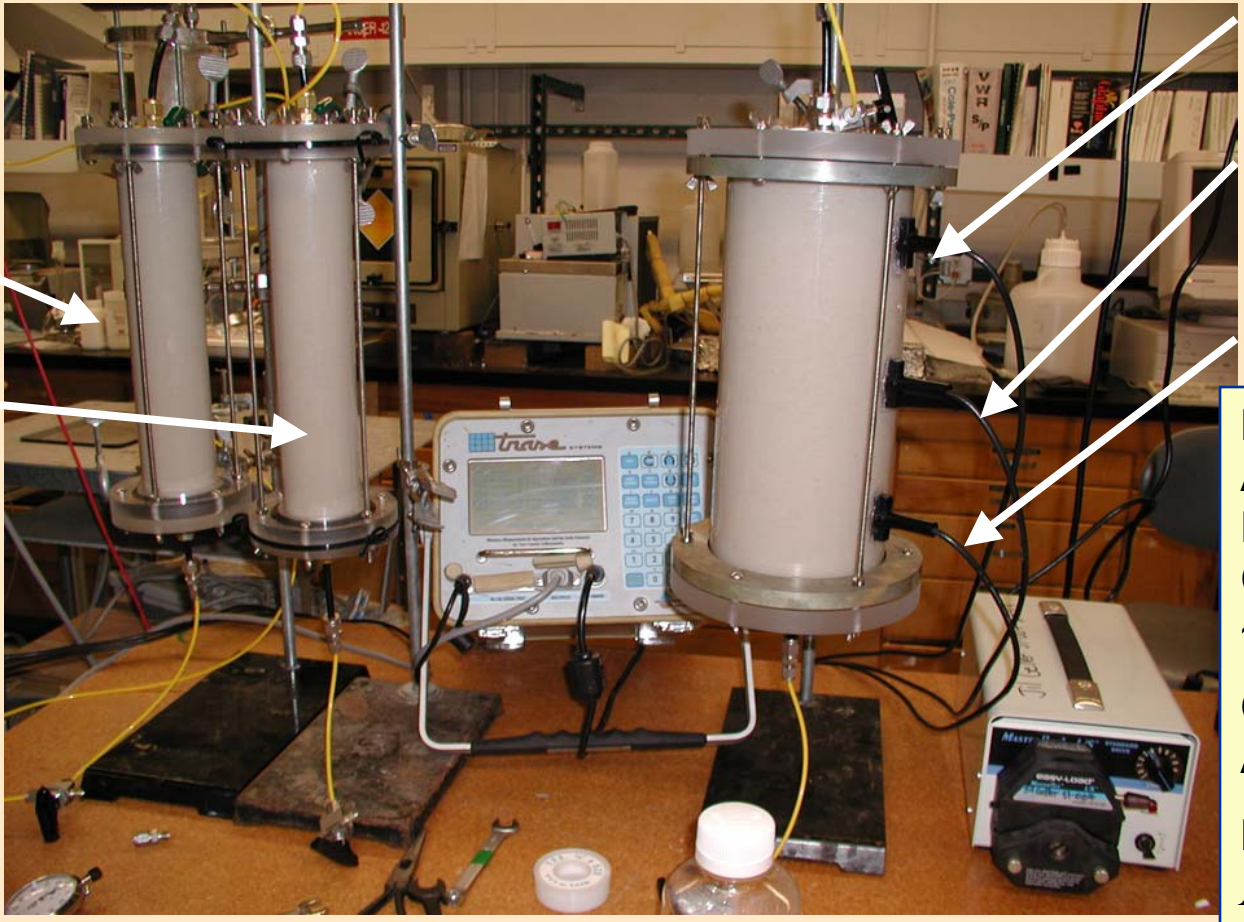
Evaluate seismic signal amplitude as a function of gas production

***K measured using constant head tests**

*** Gas sampling of evolved N_2**

Ken Williams with assist from Mary Firestone (UCB) and Fred Brockman (PNNL). In preparation for *ES&T*

Preliminary Radar Experiment: Monitoring of Gas Evolution during biostimulation of OY-107



Electron Acceptor: Nitrate, Initial Concentration ~300mg/L

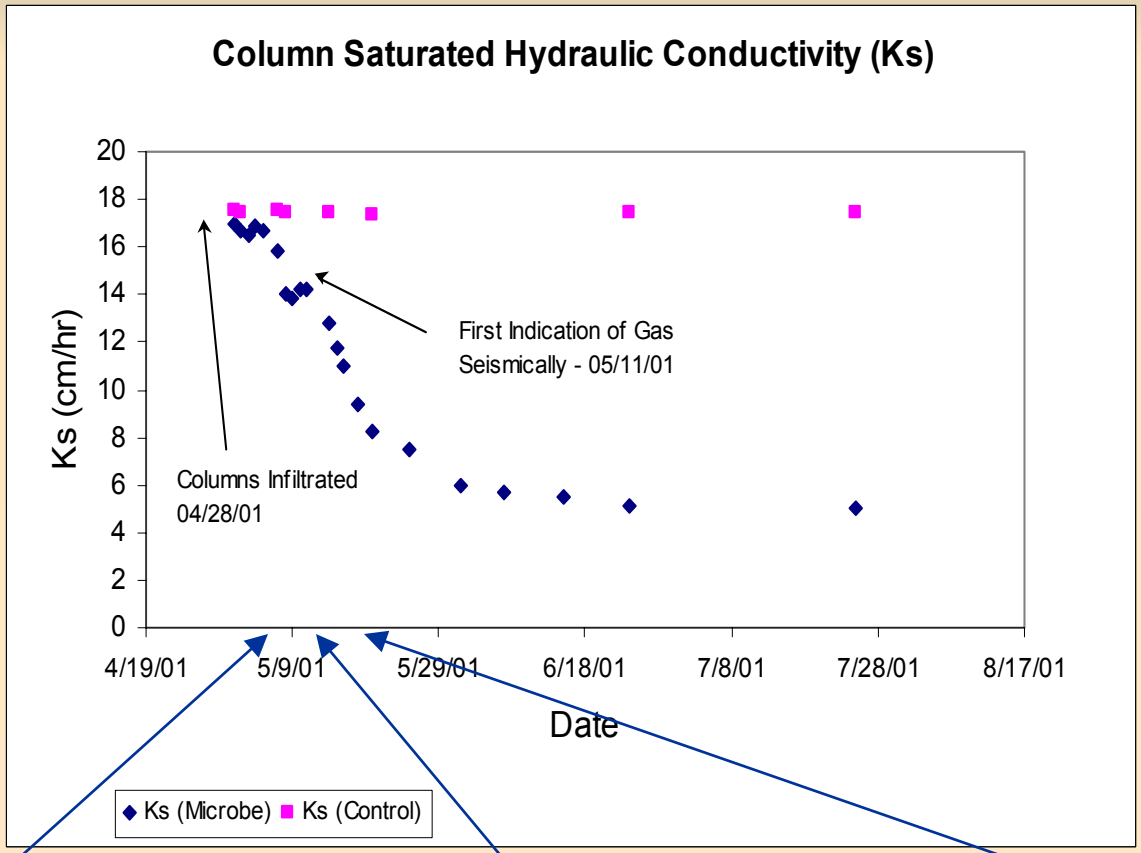
Carbon Source: Acetate

Microbe:*OY107 Acidovorax*

Grown to ~2 x 10^7 cells/gram in sand and suspended in a nutrient depleted growth media

Dielectric measurements collected every hour at each probe for 40 days

Hydraulic Conductivity and Geophysical Responses associated with N2 gas production during Stimulation



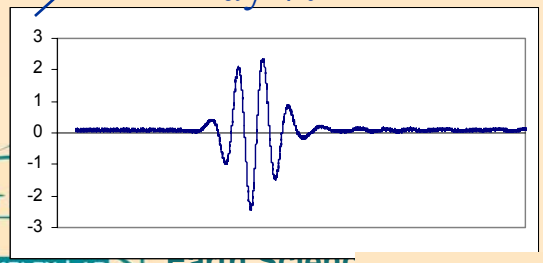
Production of gas:

** Decreased K,*

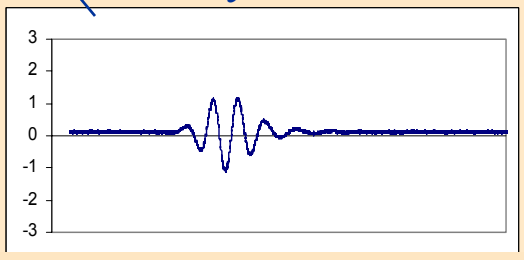
** Decreased seismic amplitude,*

** Decreased dielectric constant,*

May 7th



May 11th



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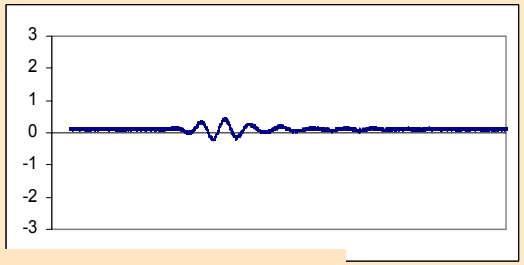
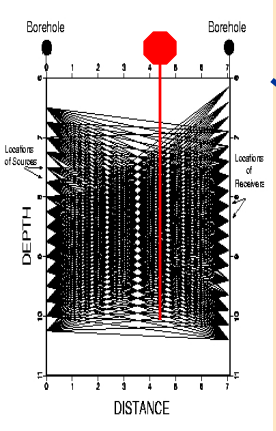
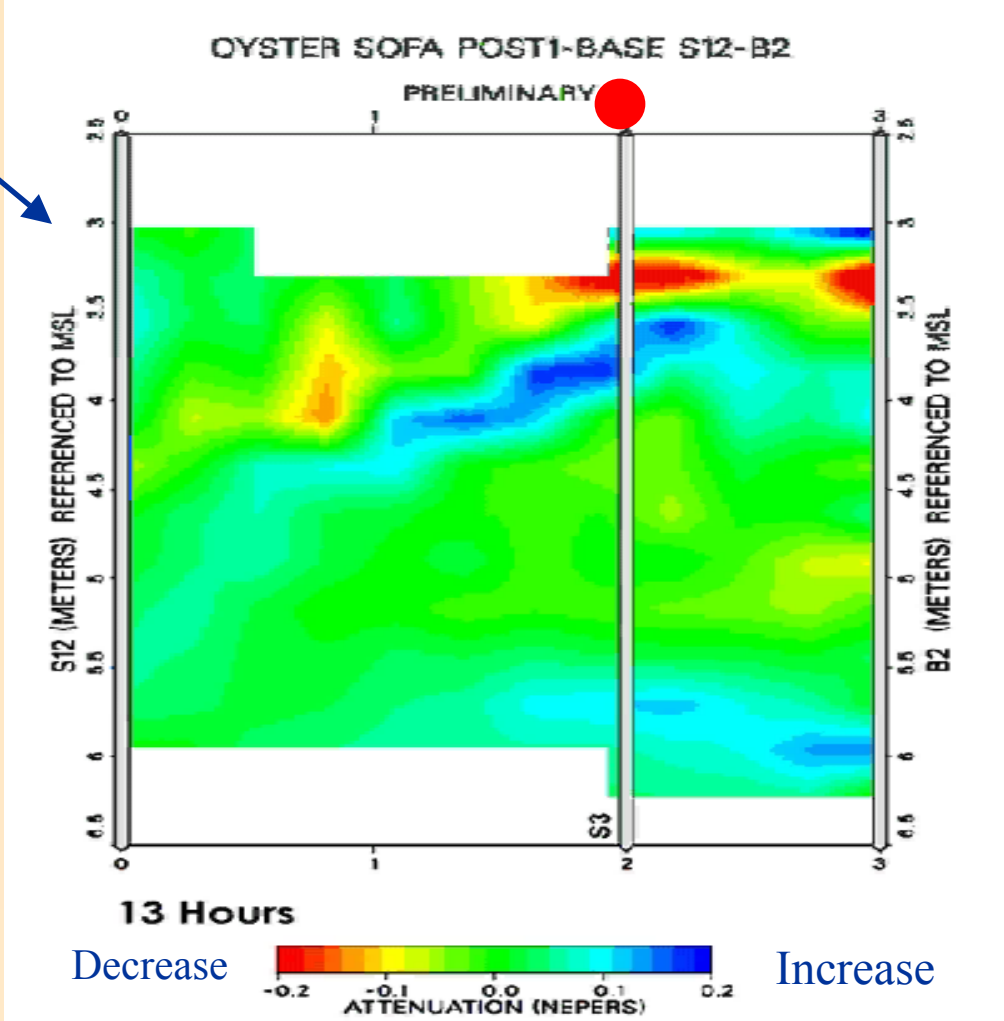


Examples of decreases in Seismic Amplitudes

Preliminary Field-Scale Biostimulation Monitoring using Time-Lapse Seismic Tomography

Lactate Injection Well





Change in Seismic Attenuation (blue=gas)

Oyster Biostimulation Experiment.
Nitrate Initial Concentration <12 mg/L (avg. 7mg/L)

Mailloux et al., *Fall AGU*, 2002

Variations in seismic amplitude correlated with N2 production near the wellbore AT THE FIELD SCALE

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EMSP NEW START: RESEARCH OBJECTIVES AND APPROACH

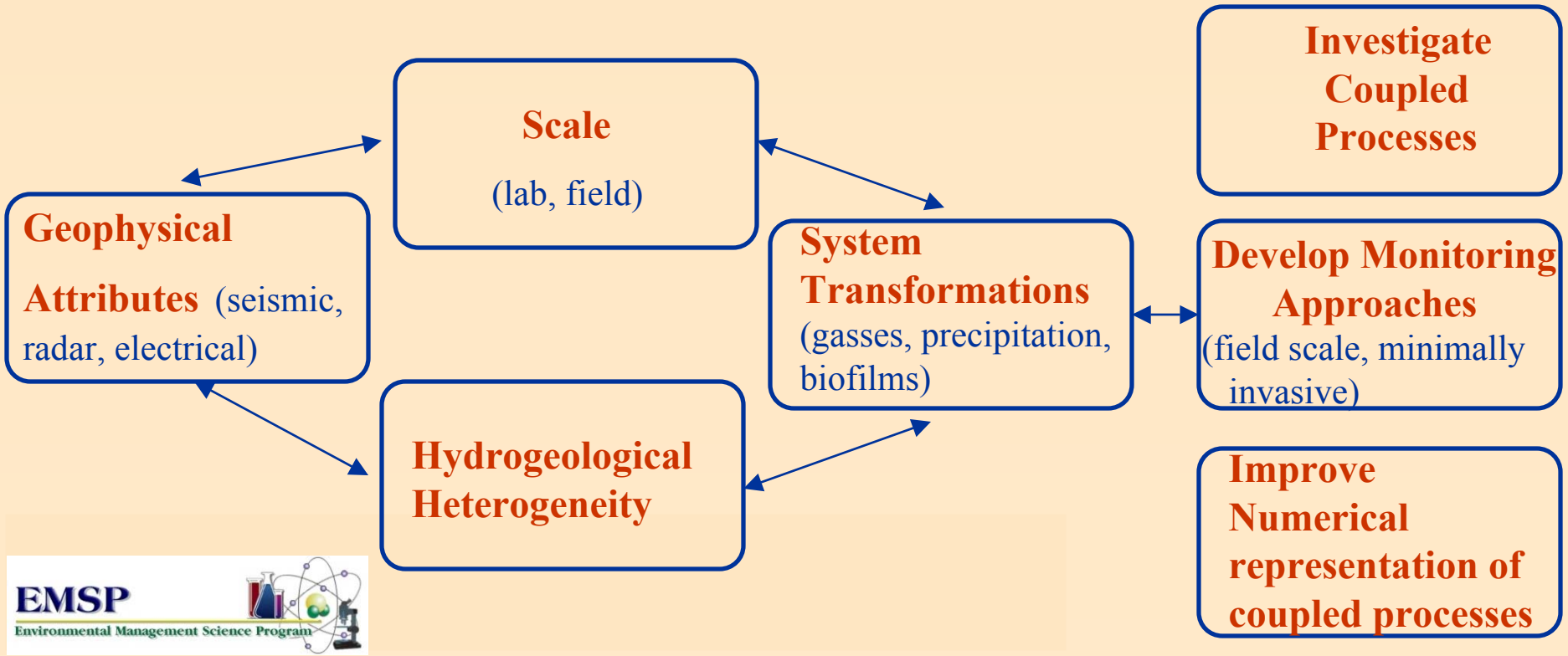
1) Understand **potential of geophysical methods** to characterize and monitor hydrogeological/biogeochemical parameters/processes:

* *at lab and field scale*
* *in the presence of natural heterogeneity*

2) Use geophysical-hydrogeological-biogeochemical data to **investigate coupled processes**:

* *onset of correlated mineralogical-biogeochemical gradients within columns*
* *interactions and dynamics of hydrological-biogeochemical alterations,*
* *microbiological induced nanopartical formation and influence on flow*

Additional: Improve representation of coupled processes in **advanced transport codes**



PROJECT TIMELINE

Lab Scale

- Column Preparation
- Numerical Modeling
- Column Measurements
  - Geophysical
  - Bioeochemical
  - Hydrological

Current

Year 1

- Lab Data Analysis
  - Estimation Methodology
  - Numerical Modeling
  - Coupled Process Investigation

Year 2

Field Scale

- Choose Field Site
- Collect Baseline Msmts. and Perform Numerical Modeling
  - Geophysical
  - Bioeochemical
  - Hydrological
- Field-Scale System Perturbation and Monitoring
- Estimate System Changes over Space and Time
- Validation

Year 3

Synthesis of Lab- and Field Studies

Developed Field-Scale Monitoring Techniques
Improved understanding of Coupled Processes

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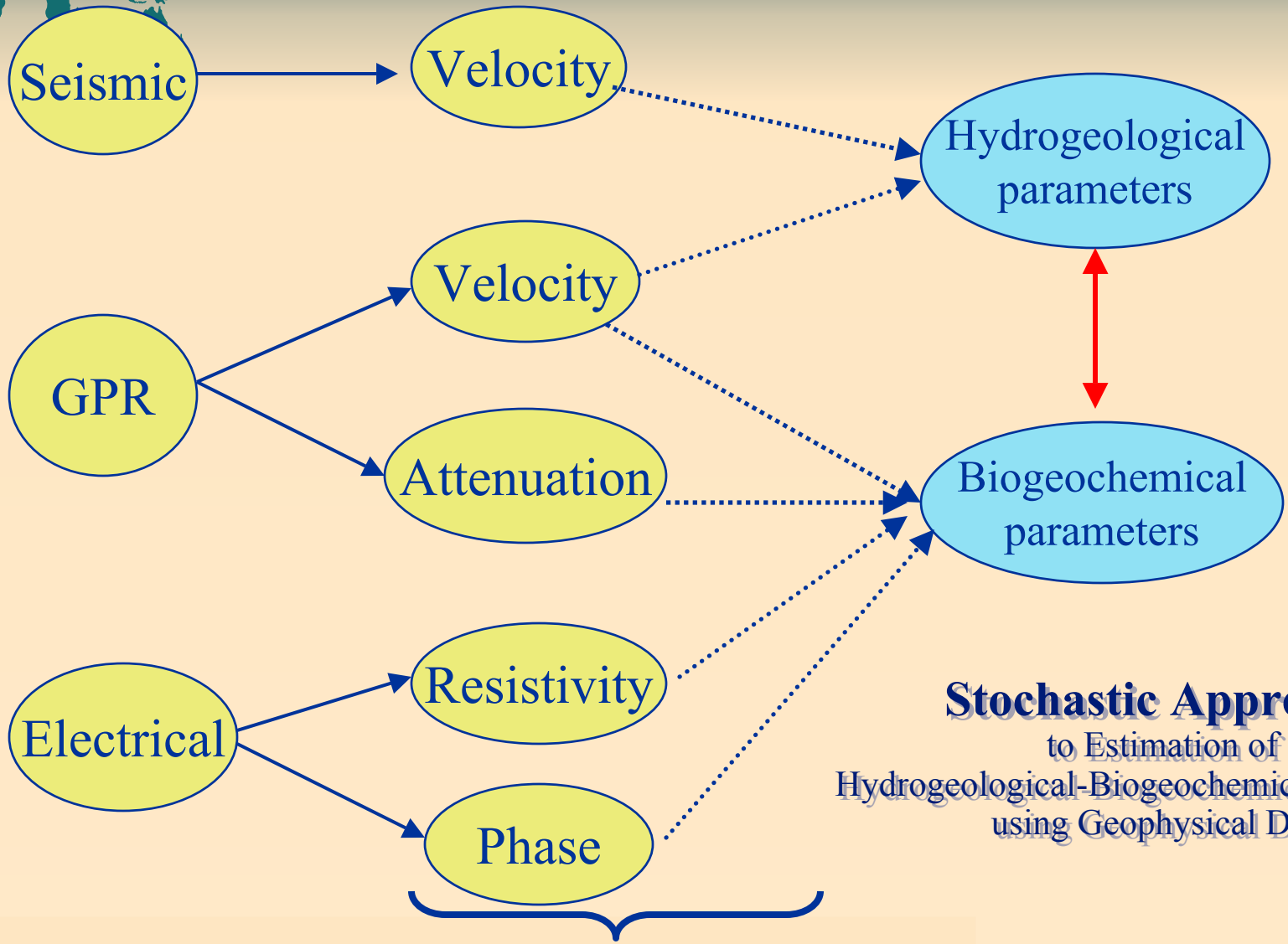
Proposed Column Experiments

CO-LOCATED MEASUREMENTS:
Geophysical (seismic, radar, electrical),
Hydrogeological, Microbiological and Geochemical -

EXPERIMENTS:

Hydrogeological Heterogeneity:	**Ideal Porous Granular Media**			**Field Sediments/GW**	
Potential Treatments:	**Low K**	**High K**	**Mixed K**	**Sieved Seds.**	**Natural Seds.**
Chemical Oxidation	X	X	X		
Biostimulation to induce precipitates, gasses and biofilms	X	X	X	X?	X?

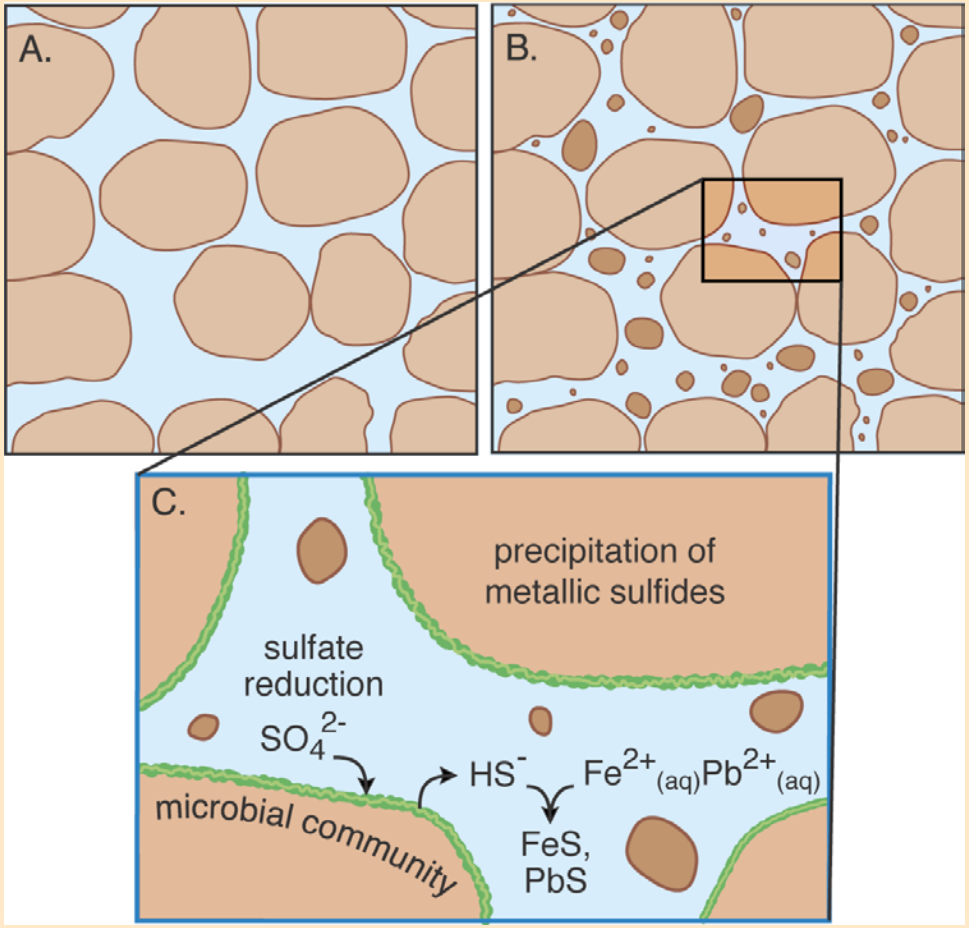
Examples: Bayesian or MCMC Approaches (Chen et al., 2002, 2001; Hubbard et al., 2001)



Stochastic Approach
to Estimation of
Hydrogeological-Biogeochemical Parameters
using Geophysical Data

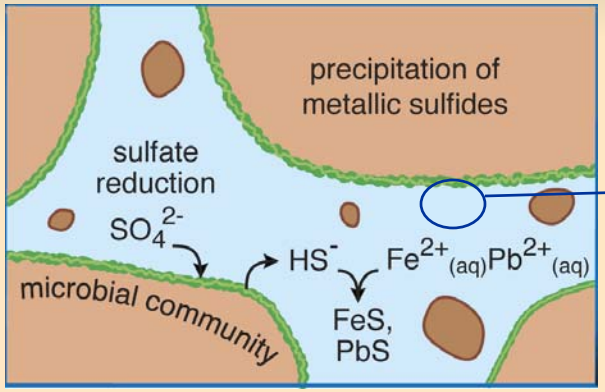
CONDITIONED TO HYDROGEOLOGICAL / BIOGEOCHEMICAL "POINT" MEASUREMENTS

Experiment Series #1: Microbe-Induced Sulfide Precipitation in Porous Granular Media



- ***Controlled Conditions:***
- **Well-defined, saturated sediments of *known* grain size**
- **Introduction of *single* microbial strain**
- **Infiltration using *defined medium* with fixed substrate and metal concentrations**
- ***Fixed* rate of advection**

Experiment Series #1: Microbe-Induced Sulfide Precipitation in Porous Granular Media



60x Optical Microscope Live/Dead Image

- ***Desulfovibrio vulgaris (ATCC 29579)***
  - Common soil borne and aquifer SRB
  - Moderately aerotolerant; no significant reduction in cell numbers after ~4-6hr of O_2 exposure
  - Parallel studies being conducted at LBNL/UCB (Genomes to Life)
  - 0.8 x 1.0um in size; free-living growth habit in liquid culture conditions / possible biofilm formation in granular medium

Widdel et al., The Prokaryotes, 1992.

Experiment Series #1: Microbe-Induced Sulfide Precipitation in Porous Granular Media

Expected Stoichiometric Reactions:

1) SRB reduces sulfate while oxidizing lactate to acetate:

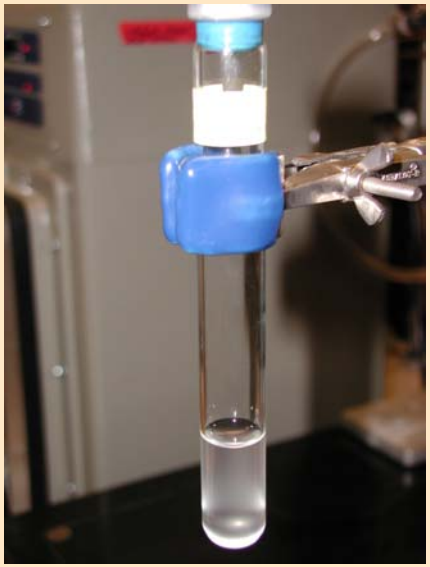
$$2CH_3CHOHCOO^- + SO_4^{2-} \rightarrow 2CH_3COO^- + 2HCO_3^- + 0.5H_2S + 0.5HS^- + 0.5H^+$$

2) Generated bisulfide reacts with metals to form metal sulfides:

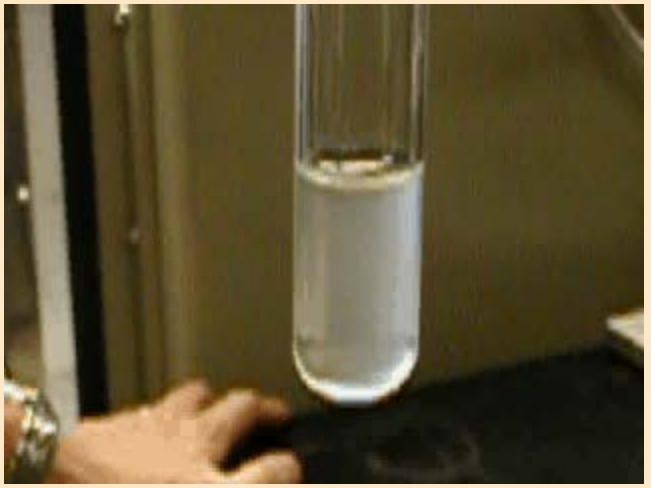
$$0.5Fe^{2+}, 0.5Pb^{2+} + 0.5HS^- \rightarrow 0.5FeS, PbS + 0.5H^+$$

Composite Reaction:

$$2CH_3CHOHCOO^- + SO_4^{2-} + 0.5Fe^{2+}, 0.5Pb^{2+} \rightarrow 2CH_3COO^- + 0.5FeS, PbS + 2HCO_3^- + 0.5H_2S + H^+$$



Liquid culture of *D. vulgaris* after 3 days on defined medium (~10^8 cells/mL)

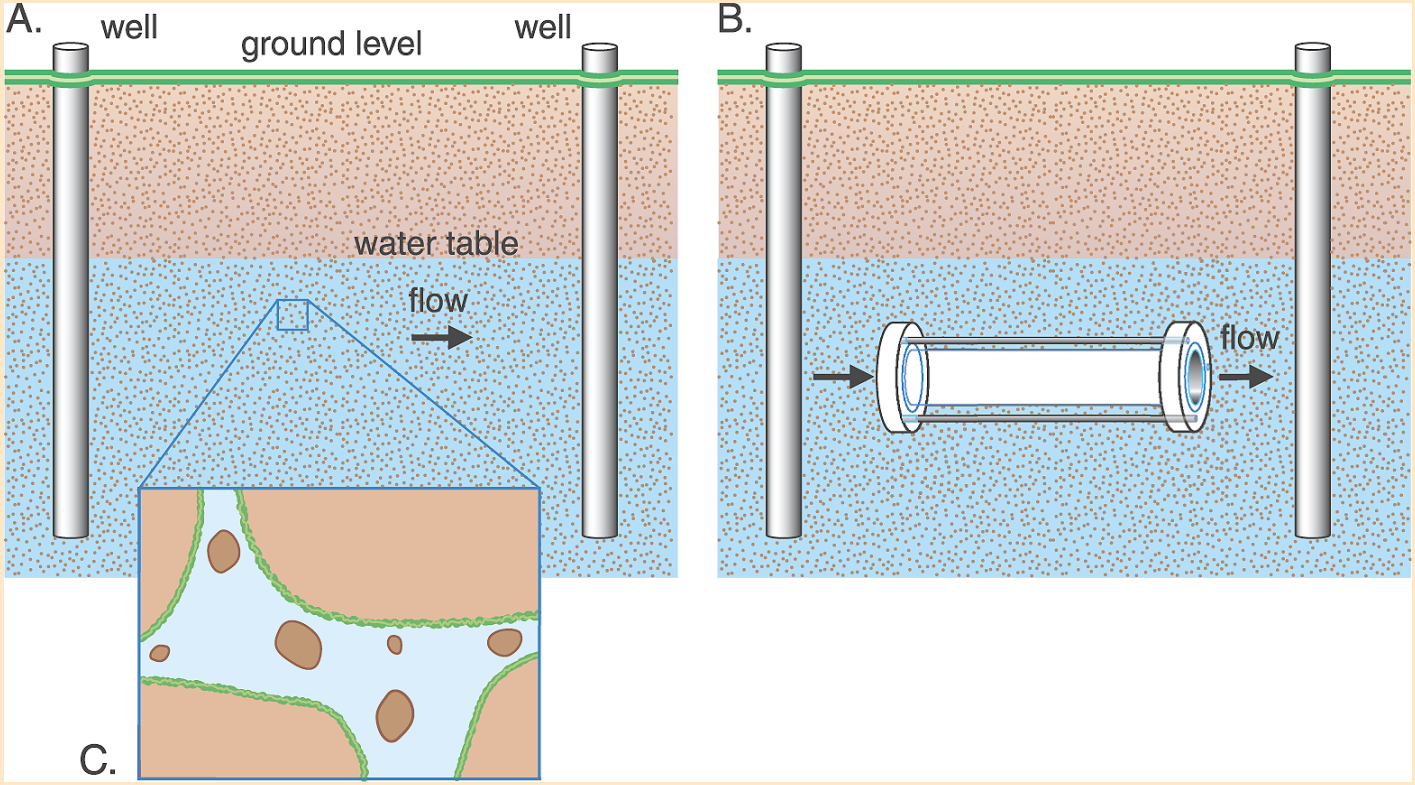


Addition of 70ppm Fe^{2+} (aq)

Rapid production of Metal Sulfides under Stimulated Conditions!!

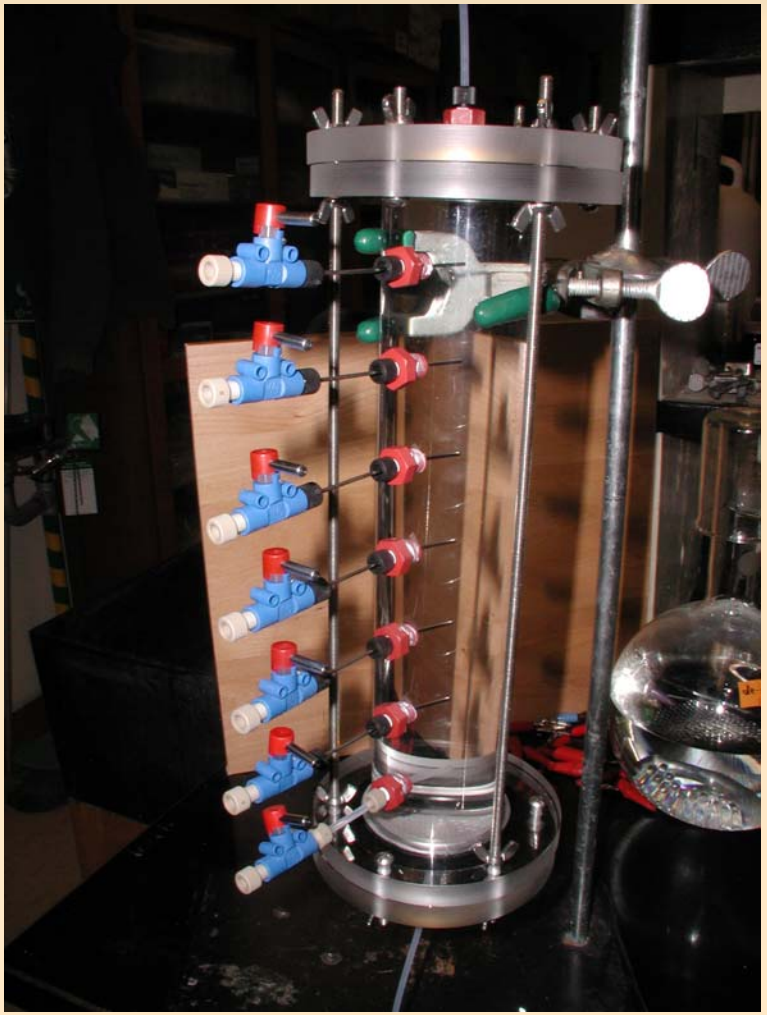
Experiment Series #1: Microbe-Induced Sulfide Precipitation in Porous Granular Media

Mimic Subsurface Using Flow-Through Column Experiments:



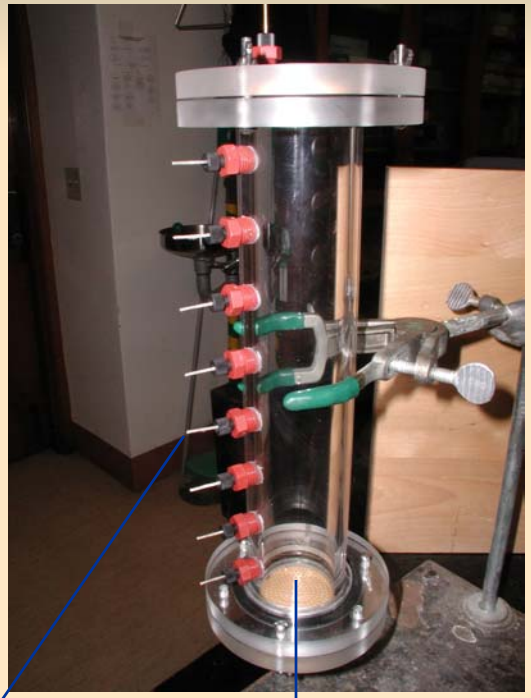
Experiment Series #1: Microbe-Induced Sulfide Precipitation in Porous Granular Media

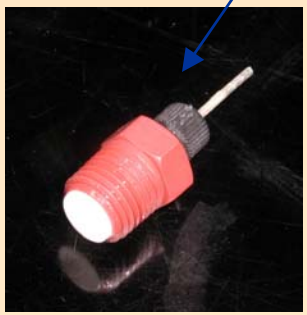
- ***Simultaneous Measurements on Control and Innoculated Columns: Biogeochemical, Hydrological and Geophysical***
  - **Multiport Biogeochemical Sampling:**
    - Fluid chemistry (anions, cations, metals, pH) using ion chromatography, ion coupled plasma, etc.
    - Biomass sampling (quantitative live/dead, PLFA)
    - Nanoparticle and/or flocculate sampling and analysis (XRD, SEM, TEM)
  - **Chemical results *directly* feed modeling effort**

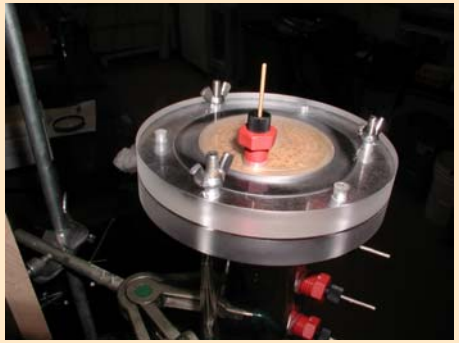


Experiment Series #1: Microbe-Induced Sulfide Precipitation in Porous Granular Media

- ***Simultaneous Column Experiments (cont'd.)***
  - **Hydraulic Conductivity**
  - **Geophysical Measurements:**
    - Radar
    - Seismic
    - Electrical
      - Complex Resistivity (1-10^5Hz) and Streaming potentials
        - Non-polarizing (i.e. low-noise) AgCl potential electrodes
        - Gold current electrodes

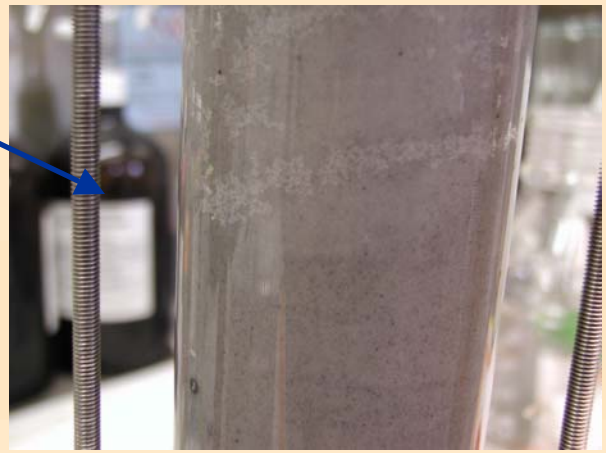






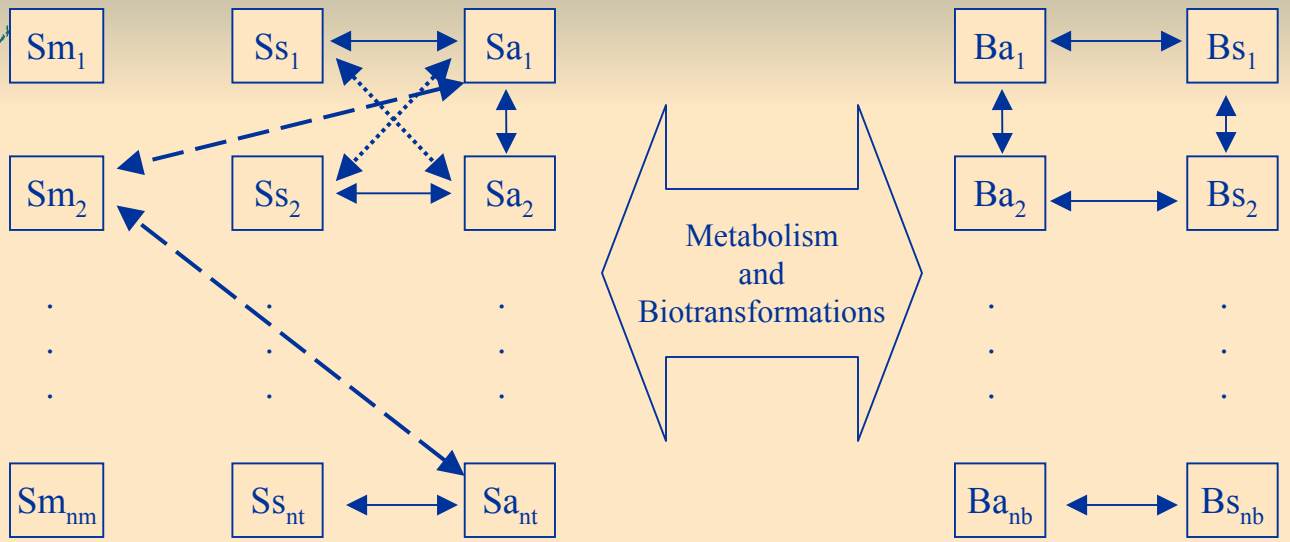
Experiment Series #1: Microbe-Induced Sulfide Precipitation in Porous Granular Media

- ***Preliminary Column Test:***
  - Flow-through of innoculum
  - Advection rate = 7cm/day
  - Non-diluted growth medium with 10ppm Fe^{2+}
  - **Observations**
    - Noticeable black precipitate (FeS) after only 2-3 days
    - Gradational precipitation front
    - Slight reduction in effluent pH (7.1 to 6.8)
    - Gas generation (CO_2, acetate?)



- ***Forthcoming Column Tests:***
  - Seismic Measurements
    - Decreases expected in amplitudes due to gases; increases expected in velocity due to increasing bulk density (mineral precipitates)
  - Radar Measurements
    - Decreases in dielectric associated with gases and possibly sulfides
  - Electrical methods
    - Changing complex electrical response and streaming potentials; increasing apparent resistivity due to precipitation of *polarizable* minerals (sulfides) and more resistive oxides
  - Hydraulic Measurement
    - Pore throat plugging (gases, minerals)
  - Biogeochemical Measurements
    - refer to modeling results...

Mechanics of Coupled Numerical Model BIOCORE (Zhang, 2000)



Sa — Aqueous chemical species

Ss — Adsorbed chemical species

Sm — Minerals

Ba — Aqueous microbial species

Bs — Attached microbial species

↔ Mass transfer between phases of given species: adsorption/desorption of chemical species and attachment/detachment of microbial species

↕ Reactions among aqueous chemical species: acid-base, redox and complexations reactions and competition, metabiosis and endogeneous respiration among microbial species

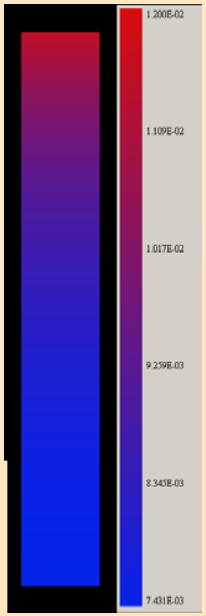
Mass transfer between phases of different species: ion exchange

Mass transfer between phases: mineral dissolution-precipitation

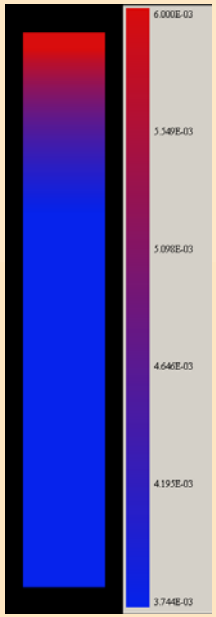
Pre-Experimental Biogeochemical Interaction Simulations using BIOCORE

	Species
Microbes	Desulfovibrio vulgaris
16 Primary Aqueous Species	H_2O, H^+, Citrate$^-$, Lactate$^-$, $SO4^{-2}$, HCO_3^-, SiO_2(aq), HPO_4^{-2}, Cl^-, NO_3^-, Na^+, K^+, Ca^{+2}, Mg^{+2}, Fe^{+2}, O_2(aq)
62 Secondary Aqueous Species	HS^-, H_2S(aq), MgHPO4(aq), CO_2(aq), $MgHCO_3^+$, NaHCO3(aq), CaHPO4(aq), $H_2PO_4^-$, $CaHCO_3^+$, $FeHCO_3^+$, $CaNO_3^+$, $NaHPO_4^-$, $MgPO_4^-$, Methane(aq), NaCl(aq), $MgCl^+$, FeHPO4(aq), $MgCO_3$(aq), $CaCO_3$(aq), $CaPO_4^-$, CO_3^{-2}, $FePO_4^-$, FeCO3(aq), $NaHSiO_3$(aq), $HSiO_3^-$, $CaCl^+$, Acetic acid(aq), $MgP2O_7^{-2}$, $NaCO_3^-$, MgSO4(aq), OH^-, $FeOH^+$, $NaSO_4^-$, $FeCl^+$, $CaSO_4$(aq), $CaP_2O_7^{-2}$, S^{-2}, PO_4^{-3}, $CaCL_2$(aq), $CaOH^+$, S_2^{-2}, $FeSO_4$(aq), H_2(aq), NaOH(aq), $HP_2O_7^{-3}$, S_3^{-2}, Acetate$^-$, $NaHP_2O_7^{-2}$, H_3PO_4(aq), $NaP_2O_7^{-3}$, $Na_2P_2O_7^{-2}$, $P_2O_7^{-4}$, $Fe(OH)_2$(aq), $H_2P_2O_7^{-2}$, S_4^{-2}, HCl(aq), $MgCH_3COO^+$, $H_2SiO_4^{-2}$, $H_6(H_2SiO_4)_4^{-2}$, $S_2O_3^{-2}$, $NaCH_3COO$(aq), Fe^{+3},
7 Minerals	Siderite, Calcite, Pyrite, Quartz, Dolomite, Greenalite, Troilite,

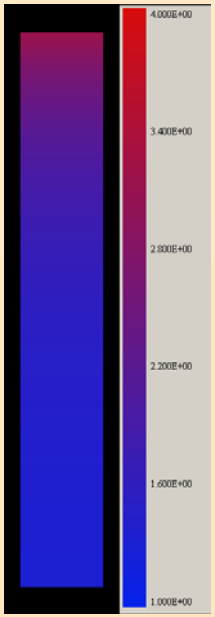
Substrate
Lactate
(mole/liter of water)



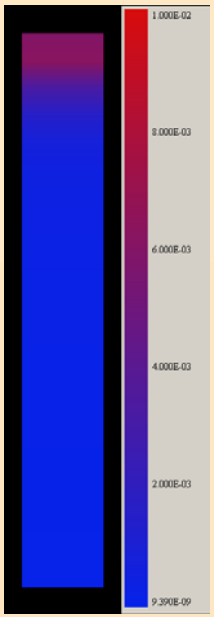
electron acceptor
Sulfate
(mole/liter of water)



Biomass
(g/liter of water)



Pyrite
(mole/liter of water)



At 4 days:
(steady state
reached at ~30 days)

Forthcoming Field Studies

- **D-Area Coal Pile Runoff Basin, SRS. Characteristics:**
  - **Contamination:** Runoff from coal storage produced contaminants (sulfate, Al, Fe, Pb,Mg, Zn..~1/2 mile from the Savannah River). Percolation of acid-sulfate waters are key concern.
  - **Geology**: Heterogeneous interbedded sand, silt, clay layers (porous granular).
  - **Hydrology:** Water table 0-15ft BGS, aquifer of interest ~45-55' BGS.
  - **Remediation:** Many remediation approaches are being considered, including sulfate reduction to immobilize metals via stimulation (Charles Turick, Michael Heitkamp, SRS).
- **Other Sites ?**

Project Summary and Expected Results

PROJECT SUMMARY

- **Components:** Theoretical, numerical, stochastic, and experimental
- **Interdisciplinary:** Hydrogeology-Geophysics-Biogeochemistry-Statistics
- **Multiple Scales of Investigation:** Lab and Field

EXPECTED RESULTS

- Potential of using **geophysical methods as a minimally invasive, cost-effective, and field-scale approach** for investigating and monitoring system transformations;
- Investigate **Coupled processes** that influence contaminant transport and remediation;
- Improved representation of coupled biogeochemical-hydrological processes in **advanced numerical transport models**;
- Assist in **assessing the efficacy of remediation** at a DOE field site.

The end